THE KINETICS OF CARBON GASIFICATION BY CO_2

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INTRODUCTION

Considerable work has been done in the area of catalytic carbon gasification(1-3) and recently an entire issue of Fuel was devoted to this area.(4) And yet there is still considerable uncertainty about the basic fundamentals. Different kinetic measurements have been reported for similar systems and different theories and mechanisms appear for catalytic gasification.

The mechanism for the gasification of uncatalyzed carbon has been postulated to be a simple two step oxygen exchange mechanism (5):

$$C_f + CO_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C(O) + CO \qquad (1)$$

$$C(O) \xrightarrow{k_2} CO + C_f \qquad (2)$$

where C_f is an available active site, and C(O) is one which is occupied has been applied to uncatalyzed gasification. In this paper, it will be applied to Ca- and K-catalyzed as well. From a kinetic analysis the rate constant k_2' can be determined. k_2' is the product of the active site density and the intrinsic decomposition rate constant, k_2. It still remains to uncouple the active site density from k_2' to determine k_2.

Such an uncoupling can be accomplished by a transient kinetics experiment. Other workers have examined the transient kinetics during the establishment of steady state gasification conditions and have reported k_1 and k_2. The activation energy for k_2 of 44.8 kcal/mole seems low.(6) In this present paper, the transient kinetics are studied as a steady state gasifying system relaxes when the oxidant is suddenly removed from the system.

Under steady state conditions, in an atmosphere of CO_2, reaction (1) is driven to the right, populating all available sites and producing one CO molecule for each active site reacted. A second molecule of CO is formed when this complex decomposes. If the oxidant were to be rapidly removed from the system, reaction (1) would be shut down but the surface complex would decay with a characteristic time constant k_2, if $k_{-1}[CO]$ were negligible compared to k_2. One can estimate the magnitude of k_2 and k_{-1} using the results of Sy and Calo.(6) k_{-1} can be determined from Sy and Calo's k_1 and Ergun's (5) equilibrium constant. At 1000 K and [CO] = 100 ppm, $k_{-1}[CO] = 9.1 \times 10^{-4}$ min^{-1} and $k_2 = 1.6$ min^{-1}. Indeed $k_2 >> k_{-1}[CO]$. At sufficiently low temperatures the decay time constant in the transient experiment will be long enough to be measurable. If one were

monitoring CO, one would expect to see ideally an instantaneous decline of the CO to one half of its steady state level followed by an exponential decay of CO.

EXPERIMENTAL

TGA experiments were done with a Dupont model 951 thermogravimetric analyzer. CO_2, CO, and Ar were prepurified grade and were used without further purification. The carbon samples used were Analab's Spherocarb (-60+80 mesh), Supelco's Carbosieve S (-120+140 mesh), glassy carbon obtained from Atomergic Chemetals Corp., and a 1000°C char made from Illinois #6 coal. Research grade anhydrous K_2CO_3 was used as the source of potassium and was co-crushed with the spherocarb to make various mixtures of K_2CO_3 on spherocarb. The Carbosieve was oxidized overnight in HNO_3 to prepare carboxylic acid sites on the carbon. To prepare Ca-treated carbon this material was then ion-exchanged in an ammoniated Ca $(NO_3)_2$ solution.

For a run, approximately 50 mg of sample were loaded into the TGA. All samples were first heated under argon up to a pre-designated temperature (50°/min up to 900°C, for non-potassium samples, 20°/min up to 800°C for potassium samples). Gasification was then generally done at or below these preheat temperatures. This was done to minimize any pyrolysis effects which might occur during gasification. Mixtures of CO and CO_2 (10% CO in CO_2 was the most common) were prepared using Matheson mass flow controllers and passed into the TGA at around 300 cc/min at a pressure of 10 kPag.

The TGA data were obtained measuring sample weight as a function of time. Steady state slopes were usually measured. For the Ca samples, generally the initial rate was taken as there was rather rapid catalyst deactivation. The rate of carbon gasified, R, is defined as 1/w dw/dt where w is the weight where the slope (tangent) was drawn and dw/dt is the slope or rate of weight loss. The units of this are g/g/min or grams of C gasified per gram of material per unit time. Figure 1 is an Arrhenius plot for one sample (20% K_2CO_3 on Spherocarb) showing the effect of the CO/CO_2 ratio.

The flow reactor experiments were done in a 1 cm ID quartz flow reactor within an open ended vertical furnace. The carbon samples sat on a quartz frit, ~20μ pore size. Gas flow was about 1000 cc/min (Ar + CO_2) and was passed down over the sample. The sample thermocouple passed through a 0.64 cm OD quartz tube through the length of the reactor and was positioned just above the frit.

In order to minimize O_2 contamination, both CO_2 and Ar were passed through an O_2 scrubber. This was a packed bed (45 cm x 1.1 cm ID) of copper chromite catalyst (Harshaw Chem) operated at 150-160°C. The catalyst was activated by H_2 reduction. The bed should reduce O_2 below 1 ppm. CO was monitored using a Thermo Electron Corporation Model 48 CO analyzer. CO_2 was monitored with a Beckman Model 865 infrared analyzer.

The procedure was to charge the reactor with sample and heat to 800-850°C under flowing Ar. This established a common reference condition

for all samples. The temperature was then dropped into the range 570-670°C and 10% CO_2 was added to the gas flow. When steady state was reached, CO_2 was turned off and the decay in CO monitored as a function of time. The observed time constant for CO_2 to be swept out of the system was about 5 sec (10%-90%). The CO analyzer instrumental time constant was 30 sec (0-95%).

ANALYSIS

In order to properly reduce the TGA data, the effect of the CO/CO_2 ratio had to be taken into account. Using Langmuir-Hinshelwood kinetics and applying the steady state assumption to C(O) in reactions (1) and (2) and assuming that the number of free sites remain constant with burn off, the global surface rate for CO_2 gasification can be shown to be

$$R \equiv \frac{1}{w}\frac{dw}{dt} = \frac{k_1(CO_2)[C_T]}{1 + k_1/k_2(CO) + k_1/k_2(CO_2)} \qquad (3)$$

where R is the measured rate of carbon weight loss, (CO_2) and (CO) are the gas concentrations of CO_2 and CO and $[C_T]$ is the active site density, g active carbon per g of total carbon. An active site is either free or occupied and hence $C_T = C_f + C(O)$. Ergun(5) has shown that Eqn. (3) reduces to

$$R = \frac{k_2[C_T]}{1+(CO/CO_2K_{eq})} \qquad (4)$$

under mild gasification conditions (low T, low pressure). In Equation (4), K_{eq} is the equilibrum constant for reaction (1) which is equilibrated at these conditions. Eqn. (4) can be rearranged so that

$$(\frac{CO}{CO_2}) = K_{eq}\ k_2[C_T]\ (\frac{1}{R}) - K_{eq} \qquad (5)$$

Hence a plot of CO/CO_2 vs 1/R should yield a straight line with y-axis (CO/CO_2) intercept of $-K_{eq}$ and an x-axis $(\frac{1}{R})$ intercept of $1/k_2[C_T]$.

The author has applied this mechanism to his data from experiments on catalytic gasification by CO_2 using K and Ca as catalysts as well as experiments with no catalyst present. The CO_2 data for K_{eq} is plotted in Figure 2. The curve in Figure 2 is the published Ergun(5) value for K_{eq} multiplied by 2. In his paper he mentioned that K_{eq} can differ by a factor of 2 depending on which of two algebraic expressions he used to obtain K_{eq}. Using K_{eq}, a value of $k_2[C_T]$ $(\equiv k_2')$ can then be obtained from eqn (4). These have been plotted as Arrhenius plots in Figure 3.

For the flow experiments, two typical CO traces are shown in Figures 4 and 5 for the carbon sample and for the Ca impregnated sample. Note that in Figure 4 there is a substantial dip which occurs when the CO_2 is first turned off. This phenomenon will be discussed later. Two pieces of information were taken from each plot: the steady state value for CO_2 gasification and the rate of CO decay.

The steady state value of CO produced can be converted into the rate constant, k_2' knowing the total molar gas flow and the carbon loading in the bed. From the overall gasification stoichiometry and the molar gas flow, the observed CO concentration can be related to the moles of carbon being gasified per unit time. Knowing the initial bed weight, k_2' ($\equiv$ 1/w dw/dt) can then be determined.

If the rate of CO decay is exponential, the decay constant is the intrinsic rate constant for the decomposition of the surface complex. In most cases, at a given temperature, a small non-zero CO value was obtained in the absence of CO_2. This value was subtracted out; it was generally less than 10% of the steady state value.

The values of k_2' derived from the steady state data are shown as an Arrhenius plot in Figure 6. The data scatter about the lines obtained from the TGA work on similar samples. Also included in Figure 6 are the decay constants from the transient experiment, i.e. the intrinsic rate constant, k_2. Least square analysis yields an average value of:

$$k_2 = 10^{11.6\pm2.3} \exp \frac{-53700\pm9400}{RT} \text{ min}^{-1}.$$

(uncertainties determined for a 95% confidence limit).

DISCUSSION

The experimental values for K_{eq} (Eqn. 1) determined in this work fall quite close to the line determined by Ergun (see Figure 2). This is strongly suggestive that the equilibrium in equation (1) is <u>not</u> affected by the presence of a catalyst. This is further corroborated by the fact that after correcting for the CO/CO_2 ratio in the manner described, the four lines in Figure 1 collapse to one line in Figure 3. Ergun determined the activation energy for uncatalyzed CO_2-carbon gasification to be 59 kcal/mole. Except for glassy carbon, in the present experiments, least squares analyses on those systems with at least seven points show activation energies within 3.2 kcal of Ergun's value. Because the lines in Figure 3 are parallel to one another, the activation energy for reaction (2), the desorption of CO, is independent of catalyst. This means that the reactive surface intermediate in the catalytic cases must decompose as if the catalyst were not present i.e., it must decompose like reactive adsorbates in uncatalyzed gasification. This author interprets the parallel Arrhenius plots shown in Figure 3 for different carbon-catalyst combinations to mean that the catalyst is effectively acting solely to increase the active site density.

The observation of a decrease in CO in the transient flow experiments of about one half followed by an exponential decay strongly suggests that the two step gasification mechanism is indeed controlling. One can now determine the fraction of total carbons which are "active" ---- dividing k_2' by k_2 yields the active site density. For the uncatalyzed carbon, one obtains a value, 4.7×10^{-5} active carbon/total C. This exceedingly small value is quite unexpected. In terms of "active surface area", this corresponds to about .019% of the total BET surface area (this was obtained using 1000 m^2/g as the BET surface area of the carbon and

8×10^{-16} cm^2 as the area for an active site(7)). This is a factor less than 1/10 that of active surface measured via O_2 chemisorption of Graphon(4). For high surface area chars, Radovic et al(8) found active surface area/total surface area ~10%. These chemisorption techniques measure active carbons with respect to O_2 adsorption. In carbon gasification by CO_2 it is not the case that all the sites available to O_2 are assessible by CO_2(9). Furthermore not all of the active sites by chemisorption are active in gasification since some represent very active sites which are probably unavailable for reaction because of a stable carbon-oxygen complex while others of low reactivity will form the carbon-oxygen reaction intermediate only very slowly.

The fact that a catalytic system yielded the same k_2 strongly supports the contention that Ca (and presumably other alkaline earth as well as alkalies) catalyze the system by increasing the number of sites. It does not affect k_2, the rate constant controlling the removal of carbon atoms as CO from the lattice.

The implication of these experiments is that a simple two step oxygen exchange mechanism, although an oversimplification, can still be used to explain CO_2 gasification. The data herein are self-consistent. The steady state values for k_2' scatter about extrapolated TGA data obtained earlier for the same samples. Activation energies for k_2' are ~ 58-60 kcal/mole. Two different carbon systems which yield k_2' (c.f. Figure 6) differing by a factor of 100 yield the same k_2 (within the scatter) with an activation energy roughly the same as k_2'.

The value of k_2 can be compared to the value obtained by Sy and Calo. At 1000 K they obtain $k_2 = 1.6$ min^{-1}. In this work, at 1000 K, $k_2 = .71$ min^{-1}, fairly good agreement for a high temperature rate constant. Although the uncertainty in the activation energy is fairly large (53.7 ± 9.4) and encompasses the value determined by Sy and Calo (44.8), this author feels that a ΔE closer to that obtained from gasification kinetics[5,10], i.e., ΔE ~ 59 kcal/mole would be most consistent with the available data and the 2-step oxygen exchange mechanism.

There still remain questions regarding the interpretation of the data presented here. One problem can be seen in the Ca plot in Figure 5. After about 60% of the surface complex has decomposed, the rate of CO decrease slows down, i.e. more CO is liberated than expected for an exponential decay. Apparently another mechanism for CO release becomes appreciable; perhaps as just mentioned, complexes of lower reactivity begin to decompose.

In Figure 4, after CO_2 is turned off, the CO signal dips well below the 50% value before beginning an exponential decay. If one extrapolates back to t=0, however, it appears to intersect a CO value about half of the initial (because of the dilution effect of the Ar, the value should be 10% larger than 1/2). What appears to be happening is the following: In the case of uncatalyzed carbon, CO initially produced is scavenged by some surface species and can not escape as CO. This scavenging species becomes depleted and CO is able to escape from the bed, thus "resuming" the exponential decay. For Ca-catalyzed carbon either the species does not exist or the effect is swamped by the higher level of CO produced. The

observation of such a large dip suggests more complicated chemistry than a simple two-step oxygen exchange mechanism.

Other carbon systems also suggest more complicated chemistry. A different Ca-catalyzed carbon (Ca-impregnated spherocarb) gave entirely different results: on CO_2 removal (in the same temperature regime), the CO signal dropped to ~90-95% of the steady state value, and no decay constant could be measured. This kind of behavior was observed with K_2CO_3/spherocarb samples. The CO concentration dropped to about 90% and declined further slowly with time. In work done subsequent to that reported herein, spherocarb gave a similar rate constant as determined here but the CO fell more than half of the steady state value. The results seem to depend on the particular carbon system not on the experimental arrangement. It is not surprising that the structure of the carbon, the micro-pore distribution, the nature of the catalyst or its dispersion may have an effect on the result in these kinds of experiments.

Acknowledgements

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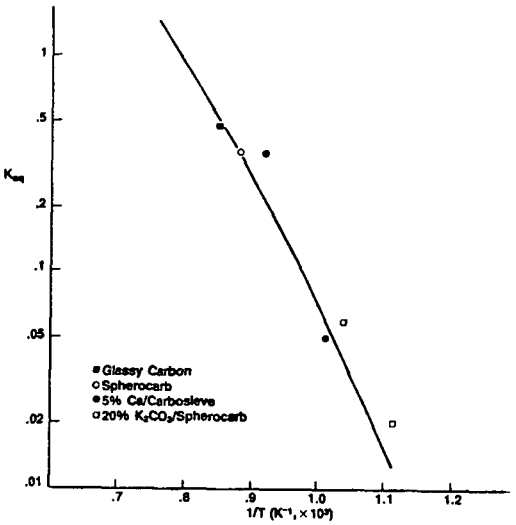

Figure 1: Oxygen Exchange Equilibrium Constant, K_{eq} as a Function of Temperature. Line is from Ergun (5), Data are from Present Experiments.

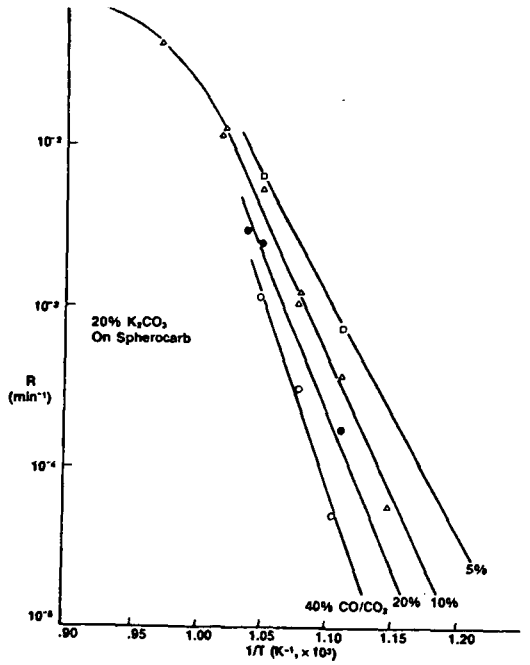

Figure 2: Effect of CO/CO_2 Ratio on Gasification Rate

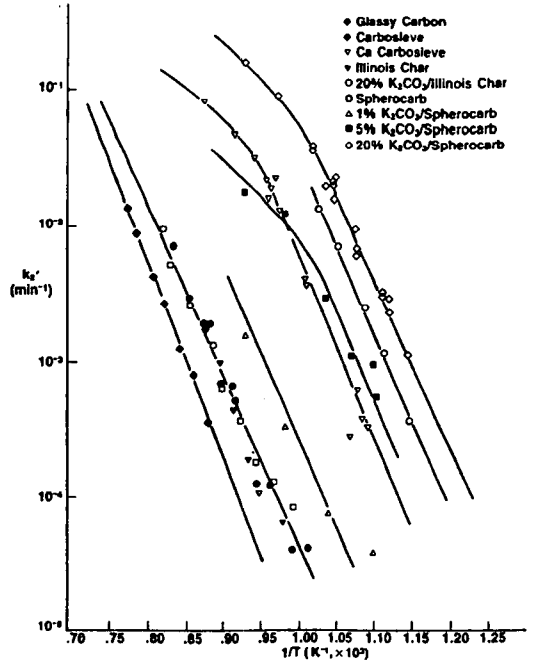

Figure 3 Arrhenius Plots of k_2 for Different Catalytic and Noncatalytic Systems.

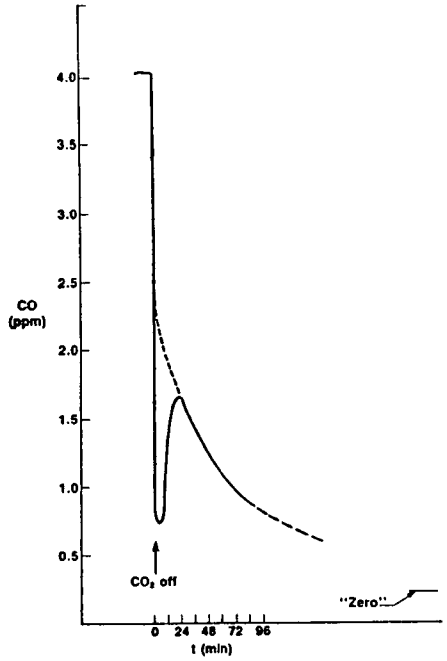

Figure 4: Experimental CO Trace for Uncatalyzed Carbon T=607°C.

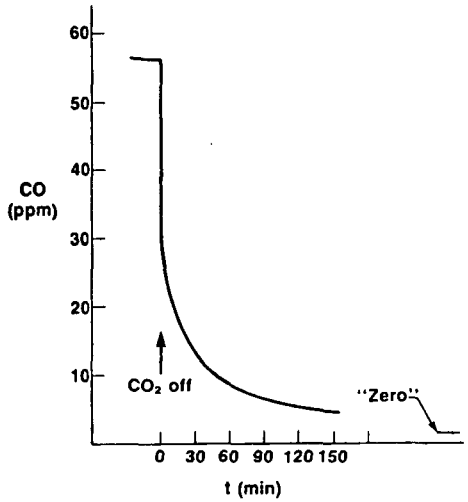

Figure 5: Experiment CO trace for Ca-catalyzed carbon, T = 629°C

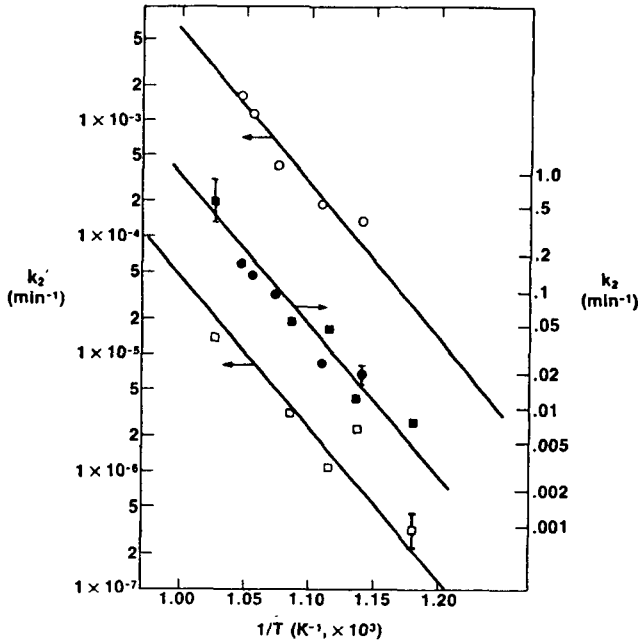

Figure 6: Arrhenius Plot of Rate Constants k_2 and k_2'; o and ○- Ca- Catalyzed Carbon; and - Uncatalyzed Carbon. The lines of k_2 are from the TGA data.